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Application of the theory of dynamical systems for nonlinear analysis of multicomponent copolymerization

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Abstract

Important qualitative features of the thermodynamic behavior of copolymers have been revealed by means of a nonlinear analysis of the dynamical equations describing their formation. On the basis of such an analysis the possibility of the synthesis of macromolecules with a periodical composition profile along the polymer chain has been theoretically predicted for the first time.

Key words: Dynamical Systems, Auto-oscillations, Nonlinear problems of chemical kinetics

1 Introduction

Copolymerization is of utmost practical importance since a great deal of synthetic heteropolymers are obtained just by this method. The polymer chain growth in the course of copolymerization may proceed via either a radical or an anionic mechanism. In the first case the time of macromolecule formation is markedly less than the duration of the polymerization process, while in the second case these time scales are comparable. It is exactly this peculiarity which is responsible for the qualitative distinctions in chemical structure

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of heteropolymers formed. The products of radical copolymerization represent a mixture of macromolecules of diverse chemical composition. This latter is characterized by the vector $\mathbf{X}(p)$ with components $X_\alpha(p)$ $(\alpha = 1, \ldots, m)$, equal to the fractions of monomeric units $\overline{\mathrm{M}}_\alpha$ of types $\alpha = 1, \ldots, m$ in polymer chains formed at overall conversion of monomers p. Many important service properties of the copolymerization products such as, for instance, their transparency and thermostability, are predetermined by the character of the evolution of a copolymer composition $\mathbf{X}(p)$ with conversion p [1] .

In order to find the dependence of $\mathbf{X}$ on p it is necessary to solve two different problems: statistical and dynamical. The first one consists in finding the vector-function $\boldsymbol{\pi}(\mathbf{x})$ which establishes the correlation between instantaneous copolymer composition and the composition of monomer mixture $\mathbf{x}$ at the moment of this copolymer formation. Vector $\mathbf{x}$ has components $x_\alpha(\alpha = 1, \ldots, m)$ equal to mole fractions of monomers M_α in a reaction system. Within the framework of the commonly accepted kinetic model of copolymerization it was shown [2] that a component $\pi_\alpha(\mathbf{x})$ of the vector $\boldsymbol{\pi}(\mathbf{x})$ is the ratio of two uniform polynomials of degree m with respect to the components of vector $\mathbf{x}$ with coefficients whose values have been tabulated for many hundreds of particular systems [3]. The last circumstance opens up fresh opportunities for the employment of the method of mathematical modeling for the optimization of the copolymerization processes. Inasmuch as $\mathbf{X}(p) = \boldsymbol{\pi}(\mathbf{x}(p))$, the task of finding the sought for dependence $\mathbf{X}(p)$ reduces to the solution of the set of ordinary differential equations

$$\frac{\mathrm{d}x_\alpha}{\mathrm{d}\tau} = x_\alpha - \pi_\alpha(\mathbf{x}) \quad (\alpha = 1, \ldots, m) \qquad p = 1 - \mathrm{e}^{-\tau} \tag{1}$$

describing the drift of monomer mixture composition $\mathbf{x}$ in the course of the copolymerization process. Examination of the character of the behavior of the solutions of this system depending on values of kinetic and stoichiometric parameters of copolymerization constitutes the essence of the dynamic problem of copolymerization.

The dynamics of anionic copolymerization is also described by equations (1) with the only distinction that here the vector-function $\mathbf{X}(p)$ will have a different meaning than in the radical copolymerization case. In the anionic process polymer chains start their growth virtually simultaneously and finish growing as soon as complete exhaustion of monomers occurs. During such a living anionic copolymerization a macromolecule length $l = l_m p$ is proportional to the conversion, where l_m is a constant equal to the ratio of overall concentration of monomers to the concentration of polymer chains. Hence $X_\alpha(i/l_m)$ is the probability for a monomeric unit, located at the distance i from the beginning of polymer chain, to be of type α. In other words the components of vector-function $\mathbf{X}(p)$ describe the profiles $P_\alpha(i)$ of the distribution of different types of units along the macromolecules. These profiles control many

properties of the products of living copolymerization including their ability to undergo phase separation [4].

Below we will present some general qualitative results of the analytical analysis of equation (1) in terms of the theory of dynamic systems and then we will proceed to a more detailed discussion of auto-oscillation regimes in the course of the processes of three-component copolymerization.

2 General results

The phase space of the dynamic system (1) is an m-simplex $x_1 + \ldots + x_m = 1$, which represents a straight line segment with unit length ($m = 2$), regular triangle ($m = 3$), regular tetrahedron ($m = 4$), etc. The drift of monomer feed composition $\mathbf{x}$ during m-component copolymerization can be presented as the movement of the point inside an m-simplex along some trajectory parameterized by the value of p or τ. When $p \to 1$ (i.e. $\tau \to \infty$) the trajectory asymptotically tends to an attractor, the simplest among which is a stationary point (SP). It was rigorously proved [5] that the number of such points inside the m-simplex can not be more than one. The same refers to SPs positioned on any k-subsimplex ($k = 1, \ldots, m-1$) lying at the m-simplex boundary. Moreover, for the coordinates of all SPs (internal and boundary ones) of dynamic system (1) simple analytical formulas were derived [1]. The type of an SP is defined [6] by the eigenvalues of the Hess matrix of the right-hand parts of equations (1) calculated at the SP at hand.

A general algorithm [2], formulated in terms of graph theory for determining the coefficients of characteristic equation of the above Hess matrix was realized as the computer program [7] enabling to find the spectrum of this matrix for the copolymerization of up to six monomers. This program provides the possibility to calculate principal statistical characteristics describing the products of multicomponent copolymerization as well as to predict some of their important properties.

3 Terpolymerization

Under copolymerization of three monomers, the vector components π_α are determined by the following formulas

$$\pi_\alpha = \frac{\Delta_\alpha}{\Delta}, \qquad \Delta = \sum_{\alpha=1}^{3} \Delta_\alpha, \qquad \Delta_\alpha = x_\alpha B_\alpha \sigma_\alpha \tag{2}$$

with

$$B_\alpha = \sum_{\beta=1}^{3} B_{\alpha\beta} x_\beta \qquad \sigma_\alpha = \sum_{\beta=1}^{3} a_{\alpha\beta} x_\beta$$

$$B_{\alpha\beta} = \begin{pmatrix} a_{21}a_{31} & a_{32}a_{21} & a_{23}a_{31} \\ a_{31}a_{12} & a_{12}a_{32} & a_{13}a_{32} \\ a_{21}a_{13} & a_{12}a_{23} & a_{13}a_{23} \end{pmatrix}$$

where $a_{\alpha\beta}$ and $a_{\beta\alpha}$ are the reciprocal values of the reactivity ratios $r_{\alpha\beta}$ and $r_{\beta\alpha}$ [3], characterizing the binary copolymerization of monomers M_α and M_β. Proceeding from the impossibility for any pair of kinetic parameters $r_{\alpha\beta}$ and $r_{\beta\alpha}$ to exceed unity simultaneously, an exhaustive classification was carried out of all types of phase portraits describing the dynamics of terpolymerization [1]. Among the 15 possible types of these portraits the most intriguing ones from the point of view of the theory of dynamic systems are those three which have no stable SPs at the boundary of the triangle (see Fig. 1). The apices of the triangle are always SPs due to the nature of the problem and the existence of SPs on the boundaries of the triangle is connected to the corresponding binary copolymerization problems. In these systems, where the kinetic parameters satisfy the inequality $(a_{\alpha\beta} - 1)(a_{\beta\alpha} - 1) \leq 0$ for all combinations of indices α and β, all SPs situated in the apices of the triangle are saddles. Consequently, the triangle sides form here the separatrix contour which can be either an attractor or a repeller for the trajectories inside the triangle. These cases correspond to negative and positive values of parameter Λ, respectively [1]

$$\Lambda = (1 - a_{12})(1 - a_{23})(1 - a_{31}) + (1 - a_{13})(1 - a_{32})(1 - a_{21}) \tag{3}$$

For the systems depicted in Fig. 1 the internal SP is not a saddle, because its Poincare index is equal to +1 [6,10]. The stability of this stationary point $\mathbf{x} = \mathbf{x}^*$, whose coordinates are determined by the expressions

$$x_\alpha^* = \frac{\Delta_\alpha^*}{\Delta^*}, \qquad \Delta^* = \sum_{\alpha=1}^{3} \Delta_\alpha^*, \qquad \Delta_\alpha^* = \omega_\alpha \sum_{\beta=1}^{3} B_{\alpha\beta}^{\dagger} \omega_\beta \tag{4}$$

with

$$B_{\alpha\beta}^{\dagger} = \begin{pmatrix} a_{12}a_{13} & a_{12}a_{23} & a_{13}a_{32} \\ a_{13}a_{21} & a_{21}a_{23} & a_{23}a_{31} \\ a_{12}a_{31} & a_{21}a_{32} & a_{31}a_{32} \end{pmatrix} \qquad \omega_\alpha = \frac{D_\alpha}{D}$$

$$
\begin{aligned}
D &= 1 - (a_{12}a_{21} + a_{13}a_{31} + a_{23}a_{32}) + a_{12}a_{23}a_{31} + a_{13}a_{32}a_{21} \\
D_1 &= 1 - (a_{21} + a_{31} + a_{23}a_{32}) + a_{23}a_{31} + a_{32}a_{21} \\
D_2 &= 1 - (a_{12} + a_{32} + a_{13}a_{31}) + a_{31}a_{12} + a_{13}a_{32} \\
D_3 &= 1 - (a_{13} + a_{23} + a_{12}a_{21}) + a_{12}a_{23} + a_{21}a_{13}
\end{aligned}
$$

depends on the sign of the real part of the roots of the characteristic equation of the Hess matrix at the SP under consideration

$$\lambda^2 + \alpha_1\lambda + \alpha_2 = 0 \tag{5}$$

This SP will be a stable or an unstable focus when $\alpha_1 > 0$ or $\alpha_1 < 0$, respectively, where the coefficient α_1 is given by formula

$$\alpha_1 = \sum_{\alpha=1}^{3} \omega_\alpha - 1 - \sum_{\alpha=1}^{3}\sum_{\beta=1}^{3} (d^*_{\alpha\beta} - d^*_{\alpha\alpha}) x^*_\alpha x^*_\beta \qquad \text{where} \qquad d^*_{\alpha\beta} = \frac{\sigma^*_\alpha B^\dagger_{\alpha\beta}}{\Delta^*} \tag{6}$$

Hence within the subspace of kinetic parameters $\{a_{\alpha\beta}\}$, where at the boundaries of the 3-simplex (triangle) only saddle SPs occur, there are two bifurcation manifolds of codimension 1 on which the rearrangements of the phase portraits take place. The first of these manifolds, $\Lambda = 0$, corresponds to the bifurcation of either the separation of the limit cycle from the separatrix contour or the confluence of this cycle with the contour. Such a bifurcation is accompanied by the change of the separatrix contour stability. The second manifold, $\alpha_1 = 0$, corresponds to the well-known Hopf bifurcation [6], when the creation or disappearance of the limit cycle happens at the moment of the change of the focus stability. Sufficient conditions $\alpha_1 < 0$, $\Lambda > 0$ have been formulated [8,1] for the existence of a limit cycle which for the dynamic system (1), (2) is always stable because the inequalities $\alpha_1 > 0$ and $\Lambda < 0$ are in this system mutually exclusive.

Let us exemplify the above formulated results by considering the particular model system where the number of external parameters is reduced from six to two, a and b, one of them being larger than unity while the other is smaller than unity

$$a_{12} = a_{23} = a_{31} = a \qquad a_{13} = a_{32} = a_{21} = b \tag{7}$$

The inner SP for this system is a focus, which is located here in the center of the triangle ($x^*_1 = x^*_2 = x^*_3 = 1/3$) and its stability is governed by the sign of the expression

$$\alpha_1 = \frac{3}{1 + a + b} + \frac{3ab}{a^2 + b^2 + ab} - 2 \tag{8}$$

The Hopf bifurcation happens here on the line

$$(2-a-b)(a^2+b^2+ab)=(1+a+b)(a-b)^2 \tag{9}$$

which can be presented in parametric form

$$a=\frac{\xi}{2}\left(1\pm\sqrt{\frac{6-3\xi}{2+5\xi}}\right) \qquad b=\frac{\xi}{2}\left(1\mp\sqrt{\frac{6-3\xi}{2+5\xi}}\right) \tag{10}$$

where the value of the parameter ξ falls within the interval $(\sqrt{3}+1)/2\leq\xi\leq 2$. Expression (3) has in the particular case under examination an extremely simple appearance

$$\Lambda=(1-a)^3+(1-b)^3 \tag{11}$$

as well as the condition of bifurcation of the change of the separatrix contour stability

$$a+b=2 \tag{12}$$

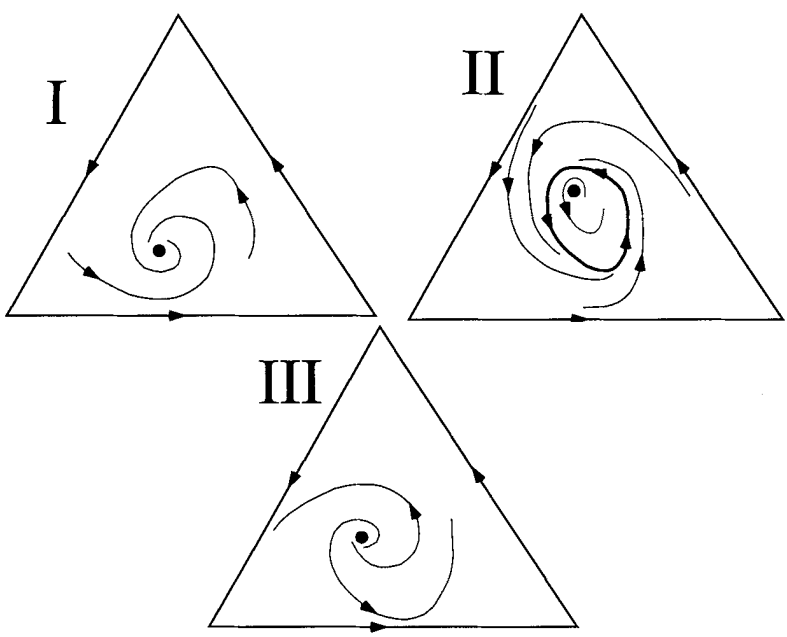

Fig. 1. Phase portraits whose classification numbers are 1 (I), 15 (II), and 2 (III) in accordance with general classification of terpolymerization dynamics [1].

The bifurcation diagram of a terpolymerization system described by two kinetic parameters (7) is shown in Fig. 2. Under their alteration, at the moment of the transition from the region (I) to the region (II), soft generation of a

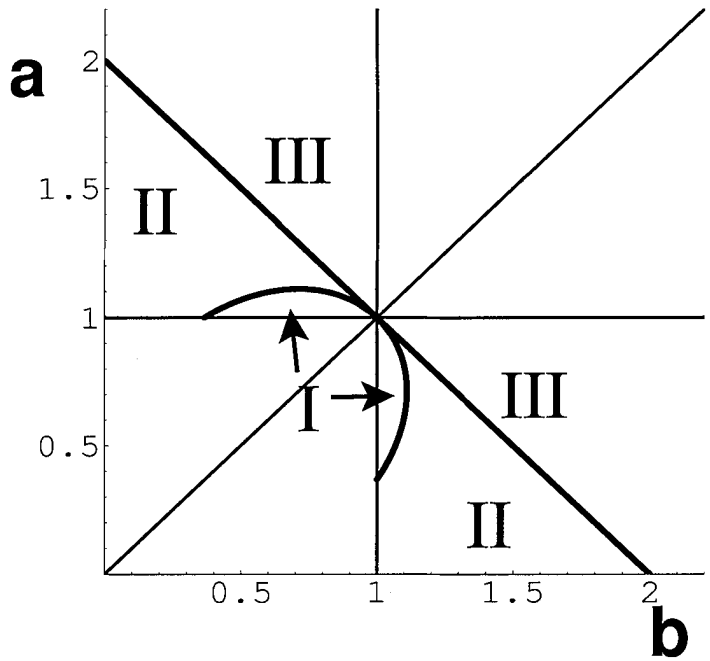

Fig. 2. Bifurcation diagram of two-parametric terpolymerization (7) inside the strips $(1 < a < \infty,\ 0 < b < 1)$ and $(0 < a < 1,\ 1 < b < \infty)$. The roman numbers indicate the types of phase portraits in Fig. 1.

stable limit cycle $\mathbf{x}^*(\tau)$ occurs, along which at $|\alpha_1| \ll 1$ the mole fractions of monomers change according to expression

$$x_\alpha^*(\tau) = \frac{1}{3} + A\sin(\omega\tau + \phi_0 + \frac{2\pi}{3}\alpha) \qquad (\alpha = 1, 2, 3) \tag{13}$$

Here ϕ_0 stands for an arbitrary phase constant, A represents small amplitude whose value is proportional to $|\alpha_1|^{1/2}$, while ω is the frequency of harmonic oscillations equal to $\alpha_2^{1/2}$. Once the expression for the coefficient α_2 of equation (5) at $\alpha_1 = 0$ is found, it is easy to get formula

$$\omega = \sqrt{\frac{2-\xi}{2+5\xi}} \tag{14}$$

describing the alteration of the frequency of harmonic auto-oscillations (13) along the curve (10). On this curve the value of ω monotonically grows from the value equal to zero on the diagonal $a = b = 1$ up to the maximum value $\omega = \sqrt{7 - 4\sqrt{3}} \approx 0.267$ at the point where one of the parameters a or b is unity, while the second parameter equals $(\sqrt{3} - 1)/2 \approx 0.366$.

The instantaneous copolymer composition in the close vicinity of the bifurcation curve $\alpha_1 = 0$ oscillates harmonically with the same frequency as the monomer mixture composition does. However oscillations of $\mathbf{X}^*(\tau)$ show

a phase lag as compared with oscillations of $\mathbf{x}^*(\tau)$, and the amplitude of the former is larger than that of the latter

$$X_\alpha^*(\tau) = \frac{1}{3} + A\sqrt{1+\omega^2}\sin(\omega\tau + \phi_0 + \frac{2\pi}{3}\alpha + \arctan\omega) \tag{15}$$

As the point on the bifurcation diagram (Fig.2) moves away from the curve (10) into the region (II) the oscillations become unharmonic, whereas the deviation of the monomer mixture and the copolymer compositions from their average values ceases to be small.

4 Anionic copolymerization

The above reported theoretical results can be employed also for describing the dynamics of "living" copolymerization proceeding by an anionic mechanism. The molecules formed will be virtually identical while their intramolecular inhomogeneity is characterized by profiles $P_\alpha(i) = X_\alpha(i/l_m)$ of the distribution of monomeric units $\overline{\mathrm{M}}_\alpha$ $(\alpha = 1, \ldots, m)$ along chains. Inherent feature of such gradient copolymers is a microphase separation leading to the formation of equilibrium spatially periodical structures [9]. The dynamic system (1) due to its nonlinearity may have several stable SPs, each possessing its own basin of attraction. A situation is conceivable therewith when two specimens of the gradient copolymer just slightly differing in average composition will have perfectly distinct profiles of monomeric units and, as a consequence, will differ substantially in their performance properties. To such a situation there evidently corresponds the case when a pair of initial points $\mathbf{x}^0$ of system (1) is positioned on either side of the boundary separating the basins of attraction of two different SPs. The above-mentioned nontrivial behavior of a copolymer system may be exemplified by the results of calculations of the terpolymerization presented in Fig. 3 for the system with three attractors, which are SPs located in the triangle apices. The qualitative distinction in the appearance of monomeric unit profiles of three specimens of copolymers just slightly differing in overall composition, depicted on this figure, results in a pronounced discrepancy in their thermodynamical properties. So, for instance, the temperature T_s, above which a terpolymer melt undergoes spinodal decomposition (responsible for the formation of spatially periodic structures) may vary essentially. For the three specimens whose profiles are presented on Fig. 3, the values of the spinodal temperature, as the calculation shows [4], equal $T_s^{(2)} = 800\mathrm{K}$, $T_s^{(3)} = 53\mathrm{K}$, and $T_s^{(4)} = 658\mathrm{K}$. These quantities are found for $l_m = 500$ at values of Θ-temperatures, $\Theta_{\alpha\beta}$, (characterizing the intensity of pair interactions between monomeric units of types α and β) given by $\Theta_{12} = 300\mathrm{K}$, $\Theta_{13} = 600\mathrm{K}$, and $\Theta_{23} = 460\mathrm{K}$.

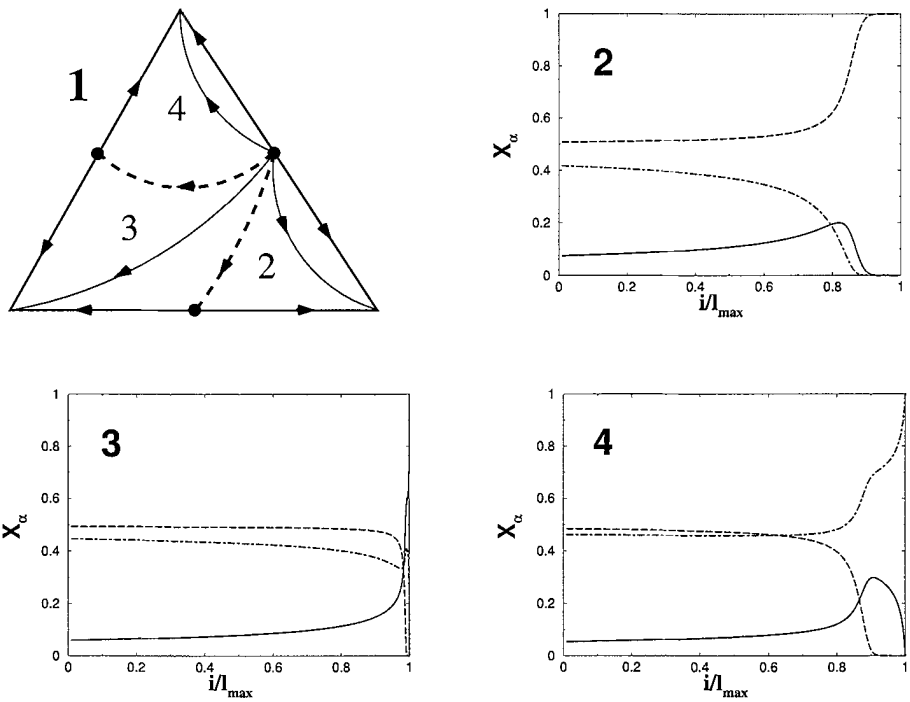

Fig. 3. The phase portrait of terpolymerization system with reactivity ratios $r_{12} = r_{21} = 1/2$, $r_{13} = r_{31} = 1/10$, and $r_{23} = r_{32} = 1/20$ (1) and the profiles of copolymer composition for initial monomer feed composition $x_1^0 = 0.1; x_2^0 = 0.5; x_3^0 = 0.4$ (2), $x_1^0 = 0.1; x_2^0 = 0.42; x_3^0 = 0.48$ (3), and $x_1^0 = 0.1; x_2^0 = 0.3; x_3^0 = 0.6$ (4). The solid line indicates monomer type 1, the dashed line monomer type 2, and the dotted line monomer type 3.

5 Conclusions

For the first time the possibility of the existence of regimes of anionic terpolymerization whose products are macromolecules with periodic composition profiles along polymer chains is predicted theoretically. The efficiency of nonlinear analysis for revealing nontrivial peculiarities of thermodynamic behavior of multicomponent copolymers is shown.

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